DYNAMIC MECHANICAL AND FRACTURE PROPERTIES OF SOME DOUBLE AND TRIPLE BASE GUN PROPELLANTS

AR-008-570

(2)

R.C. WARREN

MRL-TR-93-40

MARCH 1994

MATERIALS RESEARCH LABORATORY

DSTO

Dynamic Mechanical and Fracture Properties of Some Double and Triple Base Gun Propellants

R.C. Warren

MRL Technical Report
MRL-TR-93-40

Abstract

Dynamic mechanical tests and two types of fracture test were carried out on gun propellants of a range of compositions and made by different processes. Double base propellants, and triple base propellants containing 15%, 30% and 48% picrite, were made by the full solvent process, and one triple base propellant containing 48% picrite was made by the semi-solvent process. Dynamic mechanical and impact fracture tests were carried out on machined bars and low rate compression tests were also carried out on grains. The propellants were tested in both the as-received state and also after annealing and ageing. Filler content and annealing were found to have a large effect on the dynamic mechanical properties but these factors had a much smaller effect on fracture behaviour. No correlation between the results of dynamic mechanical measurements and fracture tests could be found. Propellant grain testing appeared to give more reliable fracture data than the impact testing of bars.

DEPARTMENT OF DEFENCE
DSTO MATERIALS RESEARCH LABORATORY

Published by

DSTO Materials Research Laboratory
Cordite Avenue, Maribyrnong
Victoria, 3032 Australia

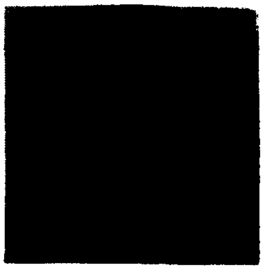
Telephone: (03) 246 8111
Fax: (03) 246 8999

AR No. 008-570

APPROVED FOR PUBLIC RELEASE

Author

R.C. Warren



Bob Warren graduated with an MSc in Physics from the University of NSW in 1968. Before joining DSTO in 1972 he worked in the fields of X-ray crystallography, neutron diffraction from titanium alloys and X-ray fluorescence spectroscopy of paints. At DSTO Salisbury he studied the mechanical properties of composite and nitrocellulose based propellants, and made significant contributions to the understanding of molecular relaxations in nitrocellulose. After a 2 year attachment in the UK he studied the rheology of nitrocellulose propellants. He is now working in Explosives Ordnance Division, Salisbury on the prediction of rocket exhaust plumes.

Contents

Dynamic Mechanical and Fracture Properties of Some Double and Triple Base Gun Propellants

1. Introduction

In the near future the manufacture in Australia of nitrocellulose(NC) based gun propellants will be changed from the current batch processes to continuous processes based on screw mix-extrusion(SME). This change will require that a detailed comparison be made of propellants made by the new and old processes to ensure that performance will not be degraded. There are a number of factors which contribute to the achievement of regular ballistic performance, and this paper will deal with one of the important factors, the fracture resistance of the propellant grains.

If propellant grains fracture during ignition in a gun extra surface area is created, increasing the rate of gas generation and hence increasing the pressure in the gun. The amount of pressure increase would vary with the brittleness of the propellant and the ignition conditions in the gun. At the very least grain fracture would cause variations in the muzzle velocity and accuracy, but in extreme cases it could destroy the gun. In this paper the term brittleness will refer to the susceptibility of a propellant to fracture in a sudden and catastrophic manner after application of mechanical stress, and toughness will refer to the ability of a propellant to resist fracture.

The fracture behaviour of small calibre ammunition can be most effectively studied directly in the gun, but this is not economical for large calibre ammunition. A laboratory scale test of fracture behaviour of large calibre gun propellants is required, with gun firings reserved for final proof. One factor facilitating the laboratory testing of large calibre propellants is the size of the grains, which are usually much larger than small calibre propellant grains.

There has been a considerable amount of laboratory testing of the fracture behaviour of large grain NC based propellants in Explosives Ordnance Division(EOD) using a variety of tests including:

1. Low rate compression of grains in the side-on mode in an Instron machine.

2. Very high rate compression of grains in the side-on and end-on modes in a Hopkinson split bar tester [1].

3. Moderate rate compression of grains in the side-on mode in a drop bar tester, which consists of a Hopkinson split bar mounted vertically with a bolt, or moving bar, dropped from a height of about 1.5 m.

4. Impact testing of notched bars in the 3 point bend mode [2,3].

5. Dynamic mechanical testing of machined bars in a Polymer Laboratories Dynamic Mechanical Thermal Analyser. The quantities measured are Young's modulus and loss tangent or tan δ.

Each test has its advantages and disadvantages, and to date no test has been selected by the international propellant community as the best predictor of gun performance. A decision on which tests are appropriate requires a number of specific issues to be considered, including:

1. The effectiveness of low rate impact testing of notched machined bars in a three point bend mode. Currently this is the most used fracture test in EOD. The bars are notched to a depth of 0.5 mm before testing, but it is possible that better results would be obtained with un-notched bars.

2. The fracture testing of propellant grains. The propellant in the grains is in the exact state in which it exists in service, and so it should be possible to relate testing of grains to performance in the gun. High rate impact testing should be used, but the load-time curves have an inertial oscillation superimposed on them which reduces the accuracy of the determination of the fracture point [2]. In this study low rate compression testing was chosen to eliminate this source of variability.

3. The possibility of obtaining a correlation between dynamic mechanical response and fracture behaviour so that extensive fracture testing could be replaced by simple dynamic mechanical test, at least for screening purposes. This possibility was mooted at least 10 years ago [4].

There are also factors relating to the propellants which need to be addressed.

1. The effect of annealing the propellants. It has been suggested that annealing at 80°C for 1 hour would significantly reduce brittleness, and that the effect would be irreversible [5]. Annealing has already been shown to have a strong effect on the dynamic mechanical properties of double base propellants, but the effect was found to be reversible [6]. Propellants often undergo a variety of thermal treatments before being presented for testing, and these differences in thermal history may affect the results. Annealing offers the possibility of producing a well defined state in the material, but annealing would only be useful if the effect was irreversible and produced a stable state in the material.

2. The effect of solvent level during processing. Manufacture by SME offers the possibility of using a wide range of processing solvent levels to gelatinise the NC. In the corresponding batch processes a high solvent level is used in the full solvent process, and low solvent levels(~3%) are used in the extrusion stage of the semi-solvent process. It is desirable to compare the fracture resistance of propellants made by both processes as an aid to designing the process for SME manufacture. In addition, the degree of gelatinisation of the NC could possibly have an effect on the behaviour of the propellants. Gelatinisation is largely affected by the strength of the processing solvent. Different solvents dissolve NC to varying degrees, and solvent strength can be varied by mixing good and poor solvents. Gelatinisation is also affected to a lesser extent by the intensity of the mixing process.

This paper reports the results of an investigation of the physical and fracture properties of a number of double and triple base propellants in an attempt to answer the questions raised above. Dynamic modulus and loss tangent were measured on machined bars of propellant. Fracture loads and energies were measured using notched and unnotched machined bars and grains of propellant. The effects of a number of factors were studied including:- manufacture by full solvent and semi-solvent processes, filler level, annealing, orientation, and degree of gelatinisation.

2. *Materials*

The composition of the double base propellant was:

Nitrocellulose(NC)(12.6%N)	53.8%
Nitroglycerine(NG)	42.5%
Stabiliser(2-NDPA)	2.9%
Cryolite	0.8%

The triple base propellants consisted of the double base matrix filled with picrite to levels of 15%, 30%, and 48% of the total weight. The last composition was similar to the US triple base propellant designated M30.

The full solvent propellants were manufactured by standard procedures, as outlined by Warren & Starks [7], which also describes the rheological behaviour of the propellant doughs. In most cases the processing solvent compositions were chosen, on the basis of experience, to give moderately poorly gelatinised propellants similar to those in service, as these present fewer problems during extrusion. However, one lot each of both the 48% filled, and double base compositions were made with stronger solvent to give well gelatinised propellants to obtain an indication to the effect of degree of gelatinisation.

The propellant doughs were extruded through 3 different dies to produce mechanical test specimens. The dies were; a slab die with section 8 mm x 38 mm, a standard 7 pin cannon propellant die with outside diameter 9.8 mm, and a single pin die with the same outside and pin diameters as the 7 pin die.

The semi-solvent propellants were made by a process which, in the initial stages, was similar to the full solvent process. The paste, acetone and about a third of the picrite were added to the incorporator and mixed for 10 minutes at 35°C. The amount of acetone was equal to the weight of NC. Mixing continued at 35°C with incremental addition of picrite until the dough was fully bound up, and then the dough was incorporated for a further 2 hours.

The dough was extruded though the die retainer plate to produce macaroni, which was dried on a rack for 1 hour at 50°C. The dried cords were then roll milled in an even speed roll mill at 40°C for 11 passes with the sheet being triple folded between passes. One carpet roll was produced and it was extruded through single and 7 pin dies at 70°C. There was insufficient material for production of slabs, and so dynamic mechanical and impact test specimens were not made.

The picrite content, degree of gelatinisation and code numbers of the propellants were:

Picrite(%)	0	0	15	30	48	48	48
Gelatinisation	Poor	Good	Poor	Poor	Poor	Good	Semi-solvent
Code number	797	808	800	801	804	807	881

3. *Dynamic Mechanical Testing*

3.1 *Experimental*

Dynamic Young's modulus and loss tangent (tan δ) of the full solvent propellants were measured as a function of frequency and temperature with a Polymer Laboratories Dynamic Mechanical Thermal Analyser (DMTA). Test frequencies were 0.33, 3 and 30 Hz, and the temperature range was scanned at a rate of 5°C/min. The specimens were bars with dimensions 6 x 2 x 30 mm which were tested in the single cantilever mode over a span of 14 mm. Two sets of bars were machined from extruded slabs; one set had the long axis parallel to the extrusion direction and was designated Axial, and the other set had the long axis perpendicular to the extrusion direction and was designated transverse, or Trans.

Specimens were tested in annealed and unannealed states. The annealed specimens were tightly wrapped in aluminium foil and placed in an oven at 80°C for 1 hour, and then allowed to cool at room temperature. Annealed specimens were tested within 1 day of annealing, and after 2 weeks of ageing at ambient temperature.

3.2 *Results*

3.2.1 *Effect of Annealing*

The peak in tan δ, which occurred at about 60°C at a frequency of 0.33 Hz, occurred at the same temperature at frequencies of 3 and 30 Hz. Figures 1 and 2 show the effect of frequency on tan δ for the unfilled propellant GP797 in the

Axial direction, and for the highly filled GP804 in the Trans direction. In both cases it can be seen that the effect of annealing at 80°C for 1 hour was to change the nature of the tan δ peak at about 60°C. The transition became frequency dependent, and it appeared to be the viscoelastic transition which had been designated "α" previously [8].

After the propellants were aged for 2 weeks at ambient temperature there was a reduction in the frequency dependence of the peak in tan δ in both the unfilled and the highly filled propellants, see figures 1 and 2. Similar behaviour was observed for all the propellants studied. The results indicate that the dynamic mechanical response of double and triple base propellants at temperatures above ambient is strongly dependent on the thermal history of the propellant, and that effects induced by changes in temperature may take weeks to diminish.

The results confirmed the previous work on double base propellants which showed that the equilibrium state of double base propellants, or triple base propellant matrices, consisted of some form of ordered structure [6]. This ordered structure underwent a melting type transition at about 55°C to a disordered structure, which was quenched in on cooling. The quenched structure showed a typical viscoelastic transition on reheating, but the ordered structure reformed after the propellant was aged for sufficient time.

3.2.2 *Effect of Filler Level*

Filler level was found to have a very significant effect on the dynamic mechanical response of the triple base propellants. Figure 3 shows the modulus and tan δ values of the propellants tested in the Trans direction at a frequency of 0.33 Hz. Only poorly gelatinised propellants are shown for clarity because the degree of gelatinisation was found to have no significant effect. The unfilled propellants had a very sharp transition above 50°C which caused the modulus to drop steeply and the tan δ to increase beyond the range of measurement. The propellant with 15% filler showed a sharp tan δ peak at about 60°C and a step in modulus at the same temperature. As the filler content increased, the magnitude of the drop in modulus and the height of the tan δ peak both decreased. Similar behaviour occurred in the Axial direction, see figure 4, but the effect of the transition at about 60°C was considerably less.

A second peak appeared at about 10°C in the triple base propellants, and it increased in height with increasing filler content. The cause of this peak was not clear but it has been previously ascribed to an interphase effect [9].

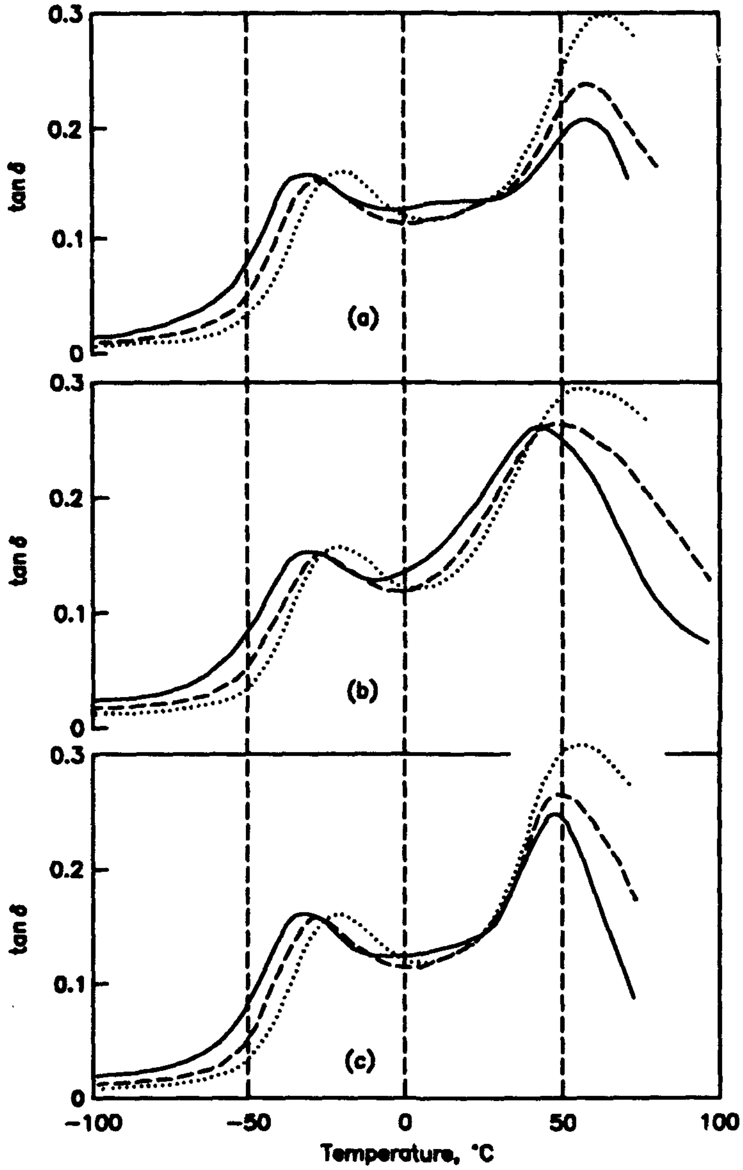


Figure 1: The effect of annealing and ageing on tan δ of unfilled propellant GP797. a. Unannealed. b. Annealed 1 hour at 80°C. c. Aged 2 weeks at ambient temperature after annealing. Frequency: [solid line] 0.33 Hz, [dashed line] 3.0 Hz, [dotted line] 30 Hz.

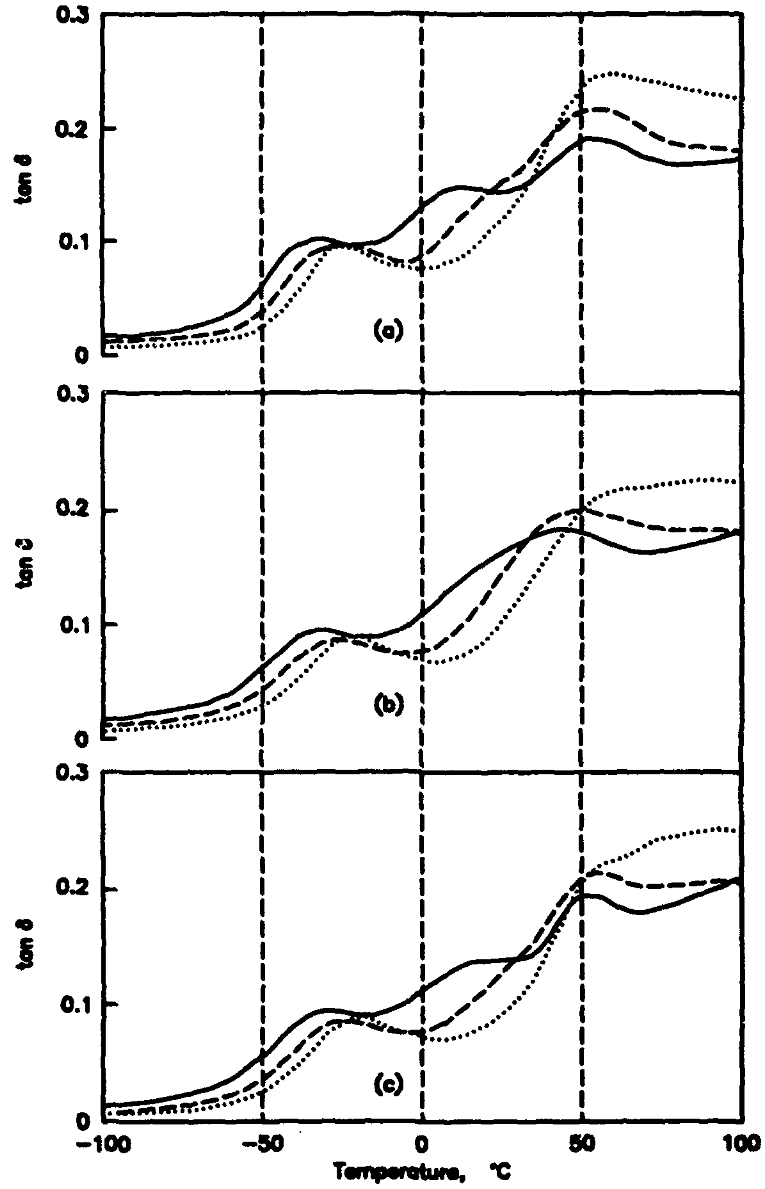


Figure 2: The effect of annealing and ageing on tan δ of 48% picrite filled propellant GP804. a. Unannealed. b. Annealed 1 hour at 80°C. c. Aged 2 weeks at ambient temperature after annealing. Frequency: [solid line] 0.33 Hz, [dashed line] 3.0 Hz, [dotted line] 30 Hz.

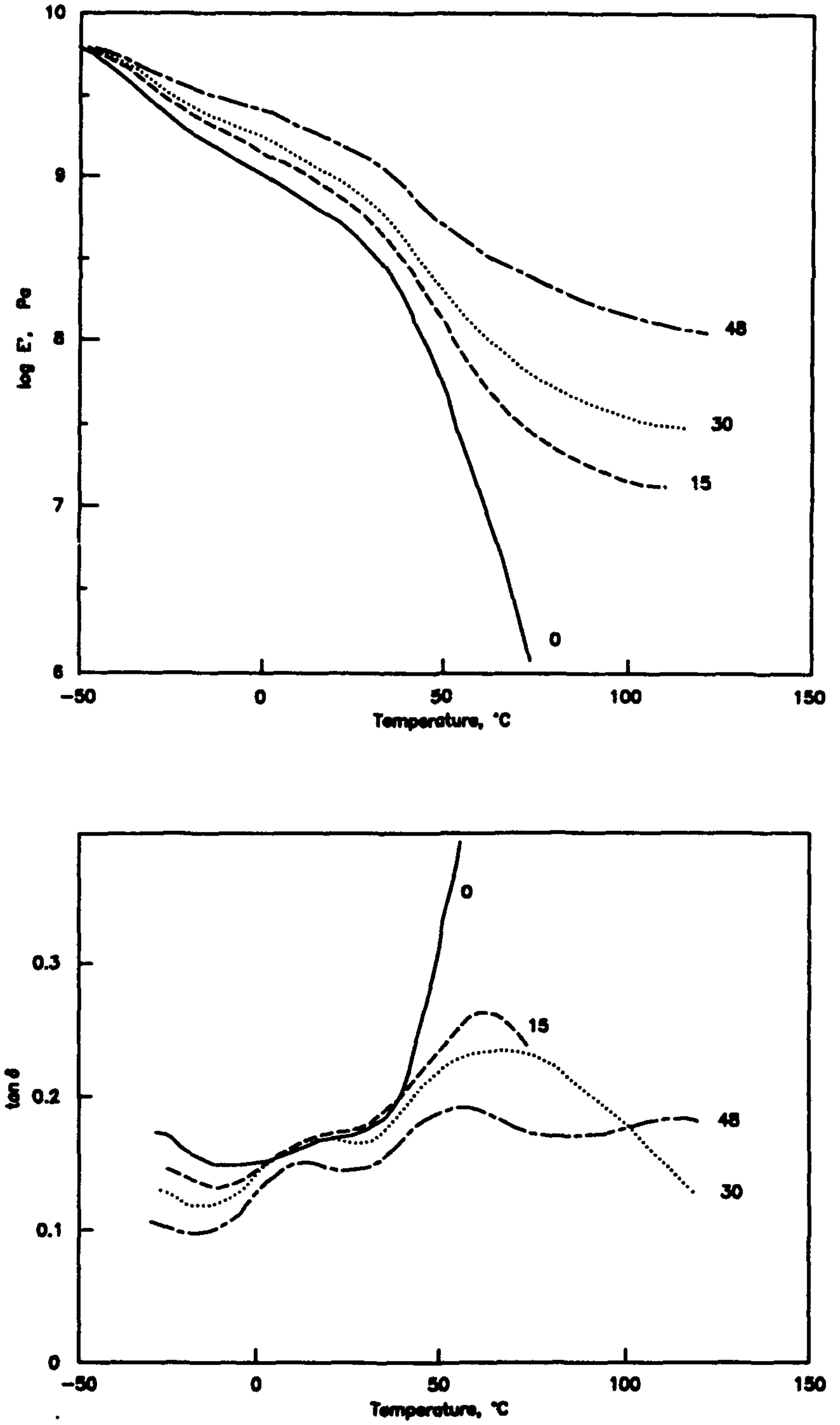


Figure 3: The effect of filler content on the dynamic mechanical response in unannealed propellants in the Trans mode at 0.33 Hz. a. Log Young's modulus vs temperature. b. Tan δ vs temperature. Picrite percentages are given by the numbers.

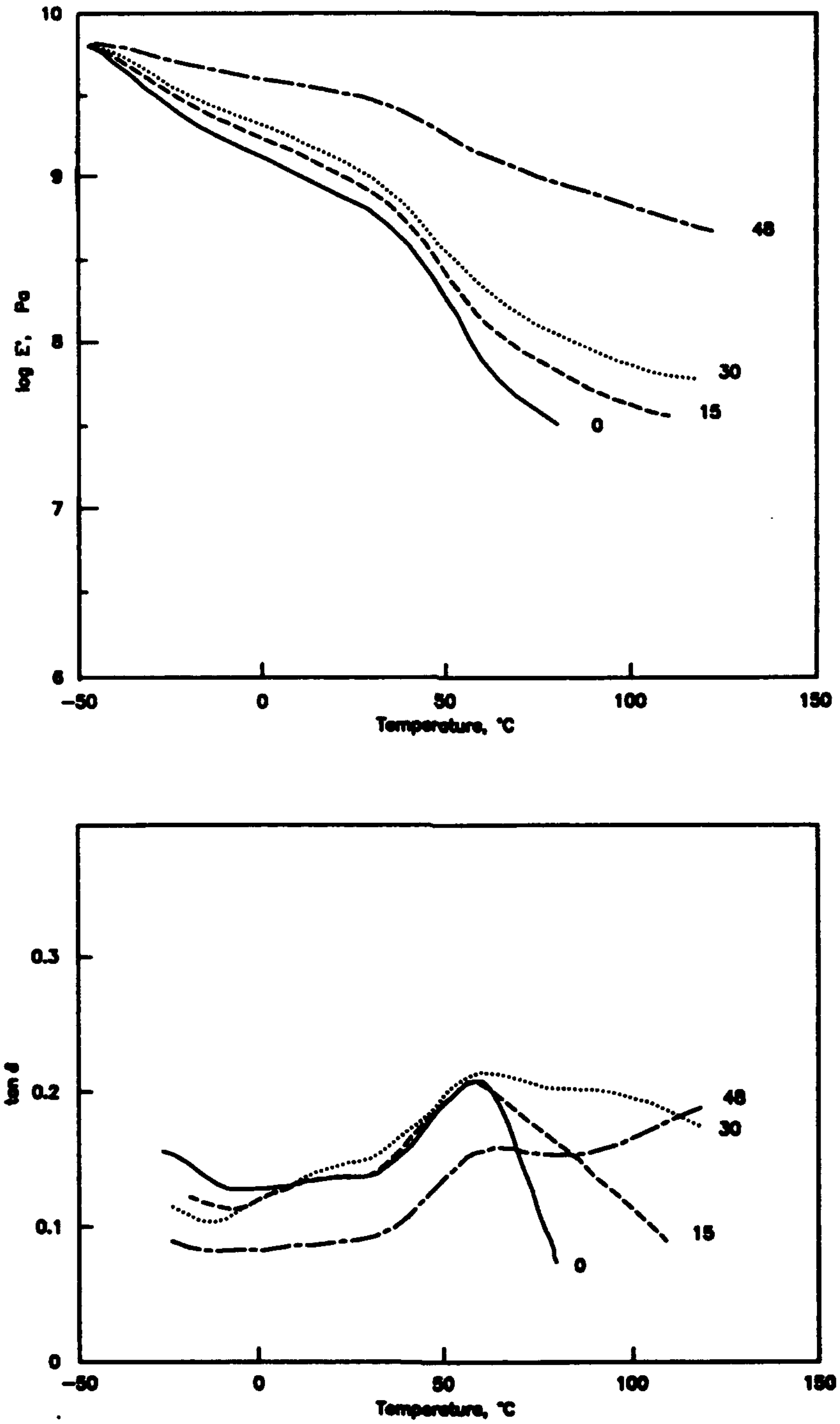


Figure 4: The effect of filler content on the dynamic mechanical response in unannealed propellants in the Axial mode at 0.33 Hz. a. Log Young's modulus vs temperature. b. Tan δ vs temperature. Picrite percentages are given by the numbers.

3.2.3 *Effect of Orientation*

Orientation also had a large effect on the dynamic mechanical response, see figures 3 and 4. The drop in modulus and the peak in tan δ at about 60°C were much greater in all the propellants in the Trans direction. The effect was very strong even for the unfilled material, which indicates that there was strong orientation of the matrix molecules.

4. Grain Compression Testing

4.1 Experimental

Single and seven perforation grains were tested at low strain rate in an Instron testing machine. The grains were machined to a length of 10 mm and mounted, with their extrusion axes horizontal, in the compression rig of the Instron testing machine. The grains were compressed across a diameter at a crosshead speed of 100 mm/minute at a test temperature of -40°C.

Specimens were tested in annealed and unannealed states. The annealed specimens were tightly wrapped in aluminium foil and placed in an oven at 80°C for 1 hour, and then allowed to cool at room temperature in a similar manner to the DMTA specimens. Usually ten unannealed grains, and 6 annealed grains, were tested at each test condition.

Seven perforation grains were also tested on the drop bar apparatus. The drop bar is a modification of the Hopkinson split bar [1]. A steel rod is mounted vertically on a fixed base, and the sample is mounted on the top surface. A bolt in a guide tube is dropped on the sample at an impact velocity of 6 m/s causing it to shatter. Load-time traces of the impact are obtained from strain gauges mounted on the side of the stationary bar, which had been statically calibrated to convert bar strain to load. Energy loss of the bolt is very small during the impact with the grain, so the velocity is considered to remain constant for the duration of the impact. Usually ten unannealed grains were tested at each test condition.

Since the grains fracture in a brittle manner, the compression load increased to a maximum, and then dropped sharply to zero after fracture. The deformation of the grain was given by the product of the crosshead speed, or bolt drop velocity, and the time of action of the load, and so the total energy was half the product of the fracture load and deformation to fracture. These parameters are dependent on grain geometry and dimensions, and hence are relative, rather than absolute.

4.2 Results and Discussion

Average values of the fracture loads and energies, and the corresponding standard deviations of all the grain tests are given in Tables 1 and 2. The effects of annealing, filler level, gelatinisation and the semi-solvent process on fracture behaviour are considered below.

4.2.1 *Effect of Annealing in Low Rate Tests of Full Solvent Propellants*

A plot of fracture load vs filler content and degree of gelatinisation for unannealed and annealed grains is given in figure 5, and the corresponding plot of fracture energies is given in figure 6. It can be seen that the effect of annealing is small, about 10%, which is of the same order as the standard deviations of the values, see Tables 1 and 2. The sign of the effect is reversed between high and low filler contents. There is not a clear statistically significant difference between the annealed and unannealed samples. In order to show the effects of other parameters more clearly, the corresponding values for annealed and unannealed propellants were averaged and plotted in figures 7 and 8 will be used in the following sections.

4.2.2 *Effect of Filler Level in Low Rate Tests*

Averaged values of fracture load and energy from both low rate and drop bar tests are plotted against filler content and degree of gelatinisation in figures 7 and 8. The poorly gelatinised propellants showed a sharp drop in fracture load and energy when the filler level reached 48%. For the single perforation grains there is no significant difference in fracture load for filler levels of 0, 15 and 30%, but there was a 20% drop in fracture energy over the same range. The seven perforation grains showed a continuous decrease in load and energy with increasing filler level.

4.2.3 *Effect of Degree of Gelatinisation*

There was no clear indication of the effect of degree of gelatinisation on fracture loads or energies. Well gelatinised unfilled (double base) propellants were significantly more brittle than the corresponding poorly gelatinised propellants, but the situation was reversed for the 48% filled propellants.

4.2.4 *Semi-solvent Propellant*

The fracture energy of the semi-solvent processed propellant was significantly lower that the corresponding full solvent processed propellants, and the fracture loads were marginally lower. These results are in line with previously reported work on semi-solvent MNF2P/S propellant [3].

Annealing increased the fracture energies of the grains by a small amount, and increased the fracture load of the single perforation grains significantly. The was no detectable effect on the loads of the seven perforation grains.

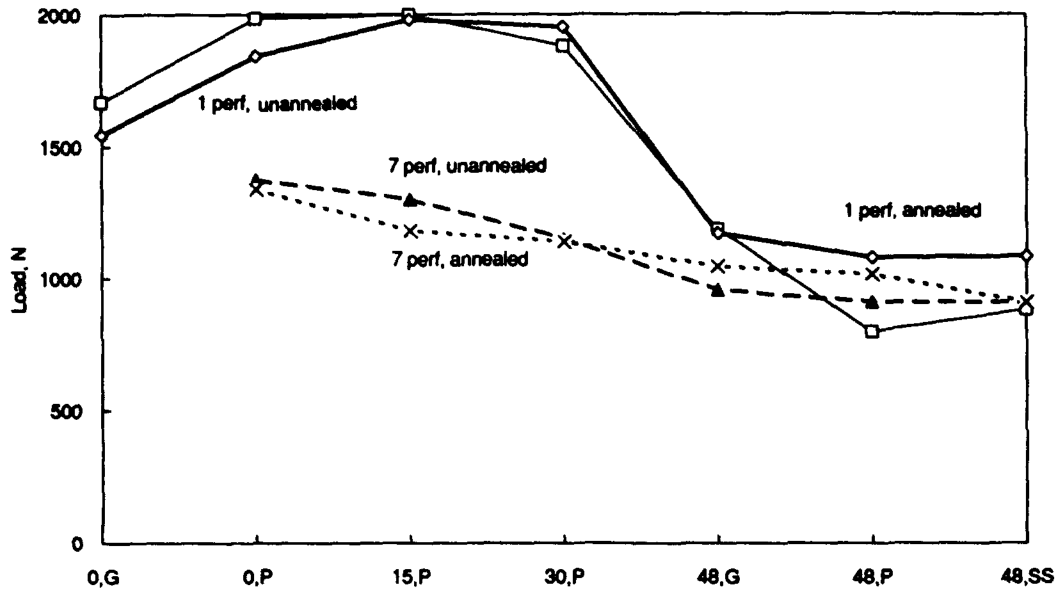


Figure 5: Fracture loads of propellant grains tested at low rates on the Instron.

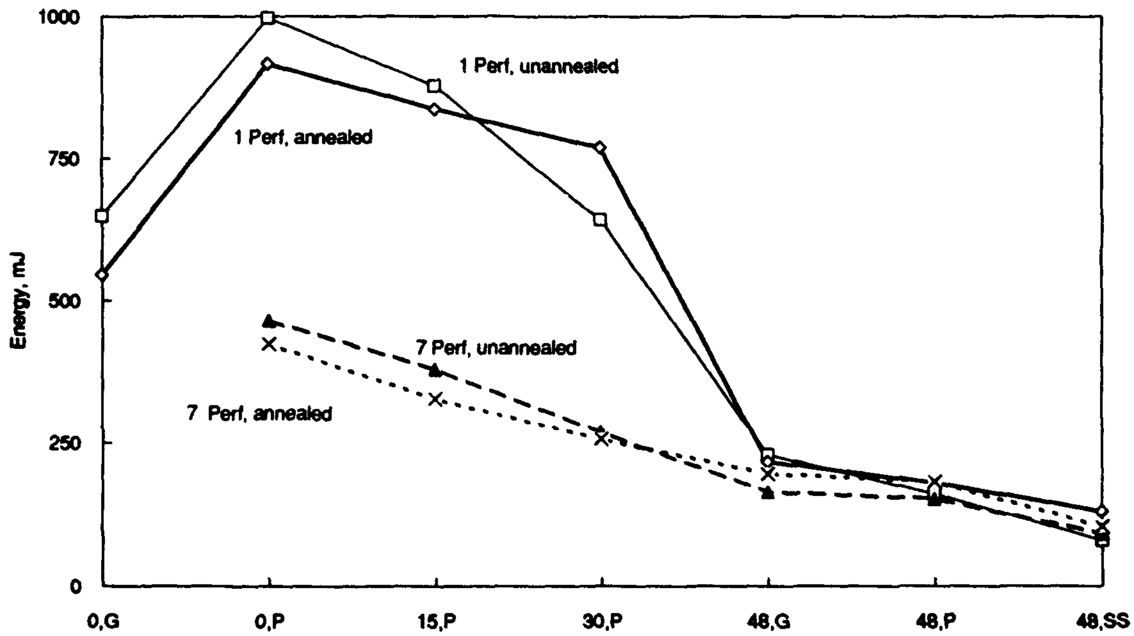


Figure 6: Fracture energies of propellant grains tested at low rates on the Instron.

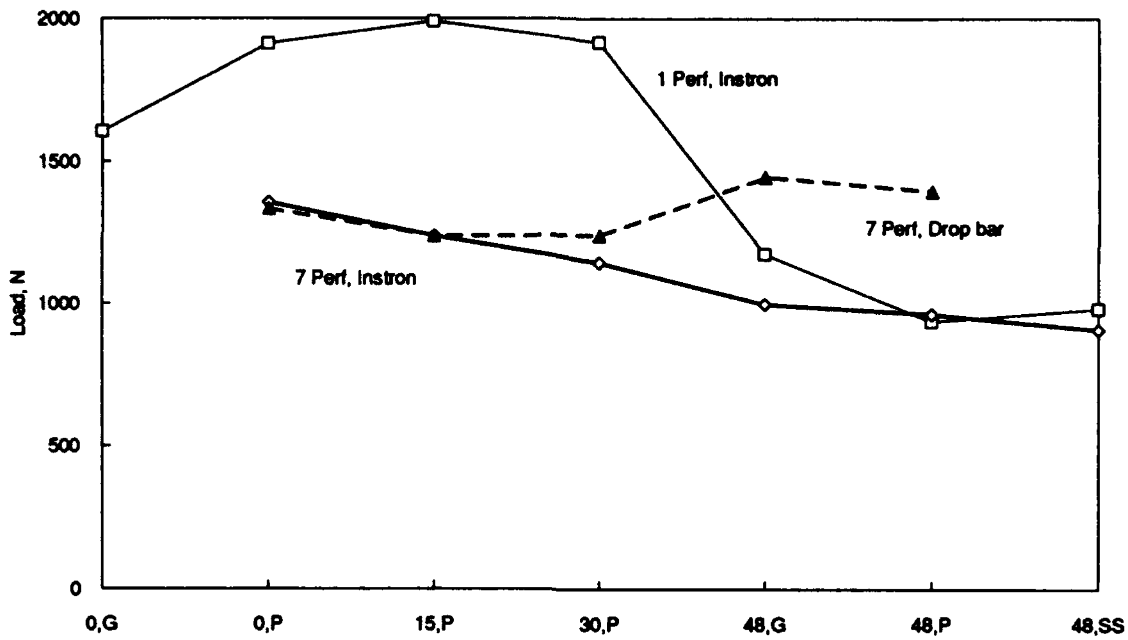


Figure 7: Average of fracture loads of combined annealed and unannealed propellant grains tested at low rates on the Instron and drop bar.

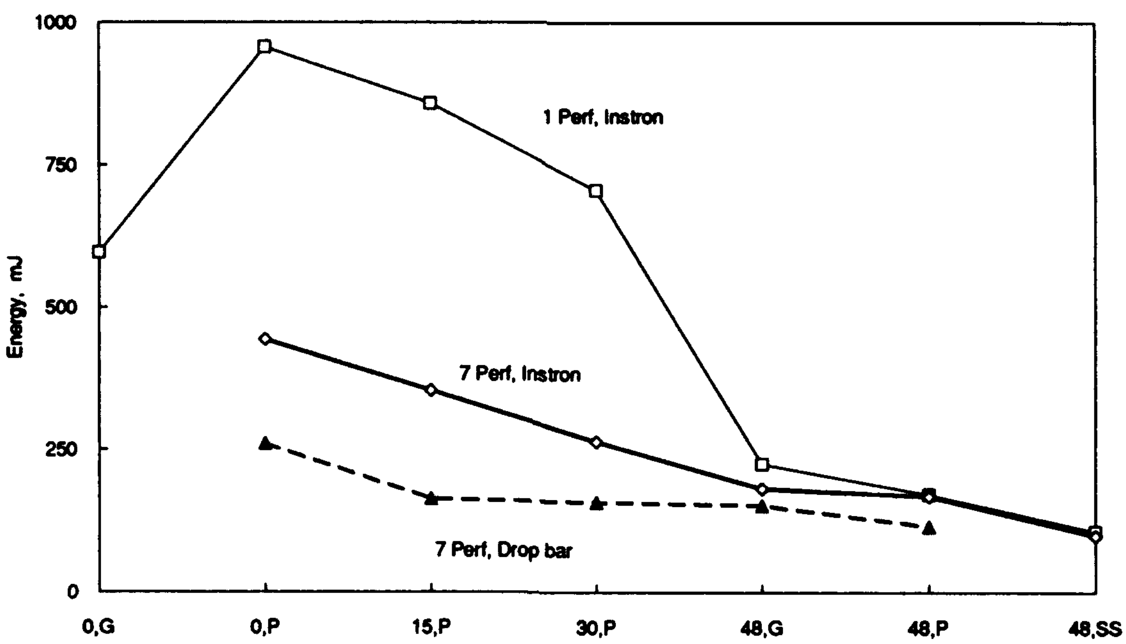


Figure 8: Average of fracture energies of combined annealed and unannealed propellant grains tested at low rates on the Instron and drop bar.

Table 1: *Fracture loads of propellant grains tested with the Instron and drop bar*

			Load (N) INSTRON				
Picrite (%)	0	0	15	30	48	48	48
Gelatinisation	G	P	P	P	G	P	Semi-sol
Code Number	808	797	800	801	807	804	881
		Single Perforation Grains					
Mean	1668	1985	1999	1880	1184	978	881
Std. Dev.	122	141	100	95	137	115	124
Std. Dev. (%)	7.3	7.1	5.0	5.1	11.6	11.7	14.1
		Annealed Single Perforation Grains					
Mean	1543	1843	1980	1953	1169	1079	1085
Std. Dev.	196	59	111	68	76	74	79
Std. Dev. (%)	12.7	3.2	5.6	3.5	6.5	6.9	7.3
		Seven Perforation Grains					
Mean		1374	1300	1150	954	911	908
Std. Dev.		96	61	91	67	102	63
Std. Dev. (%)		7.0	4.7	7.9	7.0	11.2	6.9
		Annealed Seven Perforation Grains					
Mean		1338	1180	1139	1043	1015	910
Std. Dev.		173	147	62	132	134	108
St. Dev. (%)		12.9	12.5	5.4	12.7	13.2	11.8
			DROP BAR				
		Seven Perforation Grains					
Mean		1335	1239	1241	1448	1398	
Std. Dev.		151	98	112	110	80	
Std. Dev. (%)		11.3	7.9	9.0	7.6	5.7	

Table 2: *Fracture energies of propellant grains tested with the Instron and drop bar*

			Energy (mJ) INSTRON				
Picrite (%)	0	0	15	30	48	48	48
Gelatinisation	G	P	P	P	G	P	Semi-sol
Code Number	808	797	800	801	807	804	881
		Single Perforation Grains					
Mean	648	997	878	642	231	161	80
Std. Dev.	112	104	165	96	50	34	19
Std. Dev. (%)	17.2	10.5	18.7	14.9	21.5	21.2	23.3
		Annealed Single Perforation Grains					
Mean	545	917	837	769	218	181	131
Std. Dev.	94	112	109	138	33	25	21
Std. Dev. (%)	17.3	12.3	13.1	17.9	15.1	13.7	16.4
		Seven Perforation Grains					
Mean		464	380	270	165	153	92
Std. Dev.		72	44	53	17	28	15
Std. Dev. (%)		15.6	11.6	19.7	10.2	18.6	16.6
		Annealed Seven Perforation Grains					
Mean		423	328	258	197	183	104
Std. Dev.		112	103	58	53	43	24
St. Dev. (%)		26.5	31.5	22.3	26.7	23.5	23.0
			DROP BAR				
		Seven Perforation Grains					
Mean		260	163	157	152	115	
Std. Dev.		81	40	26	27	40	
Std. Dev. (%)		31.1	24.3	16.3	17.8	35.2	

4.2.5 *Comparison of Low Rate and Drop Bar Tests*

The values of fracture energies from the drop bar test of the low picrite content propellants were significantly lower than those obtained from the low rate test, see figure 8. The relative magnitude of the difference decreased with increasing filler content, but the drop bar energies were always lower. The fracture loads showed the opposite behaviour, see figure 7. At low picrite levels the values of the fracture loads were the same, but at high picrite levels the values for the drop bar became significantly higher. Both the higher loads and lower energies may be a consequence of the rate dependence of the modulus of the propellants. The velocity of the drop bar was 3600 times the crosshead speed of the Instron, and this difference in rate would be expected to cause a significant change in modulus and fracture behaviour.

5. *Drop Weight Impact Testing of Bars*

5.1 *Experimental*

The impact testing was carried out on a Dynatup Model 8200 Instrumented Drop Weight Impact Tester. The specimens were tested in the three point bend mode over a span of 24 mm and at an impact velocity of 0.5 m/s. Specimens were bars with dimensions 6 x 6 x 30 mm which were machined from extruded slabs in the same Axial and Trans directions as the dynamic mechanical test specimens. Usually six specimens were used for each test condition, but in some cases as few as 3, or as many as 12, were used. Tests were done on both unnotched bars, and on bars with a 0.5 mm deep notch cut with a fresh razor blade at dry ice temperatures. The test temperature was -45°C.

The fracture load and energy of the bars were defined in a similar manner to the corresponding parameters for fracture of the grains.

Specimens were tested in annealed and unannealed states. The annealed specimens were tightly wrapped in aluminium foil and placed in an oven at 80°C for 1 hour, and then allowed to cool at room temperature in a similar manner to the DMTA specimens and grains.

5.2 *Results and Discussion*

Average values of the fracture loads and energies, and the corresponding standard deviations, of all the grain tests are given in Tables 3-6. The effects of annealing, filler level, gelatinisation and the semi-solvent process on fracture behaviour are considered below.

Table 3: ***Fracture loads of propellant bars tested with the drop weight impact tester***

NOTCHED BARS Load (N)						
Picrite (%)	0	0	15	30	48	48
Gelatinisation	G	P	P	P	G	P
Code number	808	797	800	801	807	804
Axial Unannealed						
Mean	245	166	171	202	270	236
Std. Dev.	18	23	16	20	13	19
Std. Dev. (%)	7.6	14.0	9.3	9.9	4.7	7.8
Axial Annealed						
Mean	187	189	148	194	284	218
Std. Dev.	13	15	12	19	19	18
Std. Dev. (%)	6.9	7.8	8.1	10.0	6.9	8.3
Transaxial Unannealed						
Mean	142	148	160	183	183	177
Std. Dev.	13	5	11	12	9	18
Std. Dev. (%)	9.5	3.4	6.6	6.6	4.8	10.3
Transaxial Annealed						
Mean	162	149	174	158	181	184
Std. Dev.	11	12	18	7	16	15
Std. Dev. (%)	7.0	7.8	10.1	4.5	8.6	8.3

Table 4: ***Fracture loads of propellant bars tested with the drop weight impact tester***

UNNOTCHED BARS Load (N)						
Picrite (%)	0	0	15	30	48	48
Gelatinisation	G	P	P	P	G	P
Code number	808	797	800	801	807	804
Axial Unannealed						
Mean	656	698	608	613	696	575
Std. Dev.	51	67	16	77	61	41
Std. Dev. (%)	7.8	9.6	2.6	12.5	8.7	7.2
Axial Annealed						
Mean	521	704	603	733	725	654
Std. Dev.	24	46	29	59	52	19
Std. Dev. (%)	4.6	6.6	4.8	8.1	7.1	2.8
Transaxial Unannealed						
Mean	421	629	483	510	356	344
Std. Dev.	53	82	35	40	66	35
Std. Dev. (%)	12.6	13.1	7.3	7.9	18.4	10.2
Transaxial Annealed						
Mean	603	635	553	569	369	368
Std. Dev.	12	47	26	15	39	20
Std. Dev. (%)	1.9	7.4	4.7	2.7	10.6	5.5

Table 5: *Fracture energies of propellant bars tested on the drop weight impact tester*

NOTCHED BARS
Energy (mJ)

Picrite (%)	0	0	15	30	48	48
Gelatinisation	G	P	P	P	G	P
Code number	808	797	800	801	807	804
		Axial Unannealed				
Mean	5.8	11.3	8.4	8.2	14.6	13.8
Std. Dev.	0.8	3.3	1.8	3.1	1.5	1.2
Std. Dev. (%)	13.9	29.1	21.2	38.1	10.1	8.9
		Axial Annealed				
Mean	12.7	17.7	8.8	10.6	25.1	10.6
Std. Dev.	3.6	3.5	1.5	2.0	4.6	0.8
Std. Dev. (%)	28.7	19.8	17.0	18.6	18.2	7.9
		Transaxial Unannealed				
Mean	8.1	10.6	8.6	8.9	6.9	8.9
Std. Dev.	0.2	1.8	1.1	2.1	0.5	1.6
Std. Dev. (%)	3.1	16.9	13.1	23.6	7.9	18.4
		Transaxial Annealed				
Mean	9.6	10.5	11.4	7.6	8.3	7.3
Std. Dev.	1.6	2.6	1.6	0.7	1.6	0.4
Std. Dev. (%)	16.2	24.6	14.2	9.9	19.9	5.5

Table 6: *Fracture energies of propellant bars tested on the drop weight impact tester*

UNNOTCHED BARS
Energy (mJ)

Picrite (%)	0	0	15	30	48	48
Gelatinisation	G	P	P	P	G	P
Code number	808	797	800	801	807	804
		Axial Unannealed				
Mean	205	215	133	133	129	79
Std. Dev.	42	48	29	29	25	8
Std. Dev. (%)	20.3	22.2	21.4	21.7	19.5	10.2
		Axial Annealed				
Mean	124	310	111	154	109	99
Std. Dev.	18	127	12	18	15	8
Std. Dev. (%)	14.6	41.1	11.2	11.5	13.9	8.4
		Transaxial Unannealed				
Mean	99	214	85	86	31	38
Std. Dev.	56	56	29	18	10	13
Std. Dev. (%)	56.4	26.1	33.8	20.4	31.0	35.4
		Transaxial Annealed				
Mean	191	209	139	138	27	30
Std. Dev.	24	38	28	8	5	3
Std. Dev. (%)	12.6	18.3	19.9	6.1	17.6	10.4

5.2.1 *Results and Discussion*

The fracture loads of notched and unnotched propellant bars are plotted in figures 9 and 10. It can be seen that for the notched bars annealing made no detectable difference, for the unnotched bars the loads increased 5-10%, which is of the order of the standard deviation of the values.

Fracture energies of the notched and unnotched bars are plotted in figures 11 and 12. For the notched bars there was a significant increase in fracture energy for some of the annealed bars tested axially, but not for bars tested transaxially. In the unnotched case the situation was reversed, with some annealed bars tested in the Trans direction showing an increase in energy, but not in the Axial direction.

Considering the data as a whole, the differences between the annealed and unannealed fracture loads and energies are within experimental error. In order to show the effect of the other parameters more clearly the corresponding annealed and unannealed values were averaged and plotted in figures 13 and 14.

5.2.2 *Effect of Filler Level*

Fracture loads and energies of the bars are plotted in figures 13 and 14. The values plotted are the averages of the corresponding annealed and unannealed values. It can be seen that filler level had a relatively small effect on the fracture loads and fracture energies of the notched bars and on the fracture loads of unnotched bars. However, there appears to be a significant decrease in fracture energy with increasing filler content for the unnotched bars in the Axial direction and a greater decrease in the Trans direction.

5.2.3 *Effect of Degree of Gelatinisation*

The degree of gelatinisation did not appear to have a consistent effect on either the highly filled and unfilled propellants, see figures 13 and 14. In the case of the unnotched bars the well gelatinised unfilled propellant was significantly more brittle that the poorly gelatinised propellant, but the opposite was true of the filled propellants. The effect was much smaller in the case of the notched propellants, and in some cases appeared to be reversed. In view of these variations no conclusions can be drawn.

5.2.4 *Effect of Orientation*

The fracture loads and energies of the unnotched bars were significantly higher for the bars tested in the axial direction than in the transaxial direction, see figures 13 and 14. The difference was greater at higher filler levels, where the effect of filler alignment is greater. The needle-like form of the picrite crystals would cause them tend to align along the extrusion axis during extrusion. When the testing is in the transaxial direction the crack can propagate relatively easily between the crystals, whereas in the axial direction the crack has to propagate across the crystals where they would have to be broken or pulled out. However, the fact that the effect was apparent in the unfilled propellants also shows that orientation of the matrix affects toughness as well.

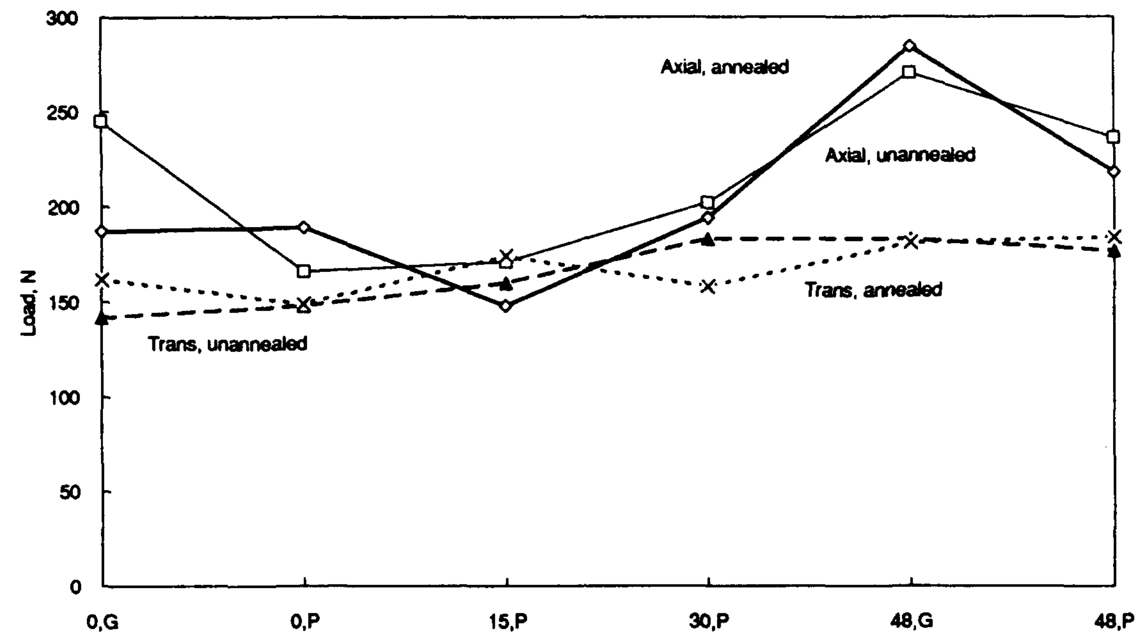


Figure 9: Fracture loads of notched propellant bars tested on the drop weight impact tester.

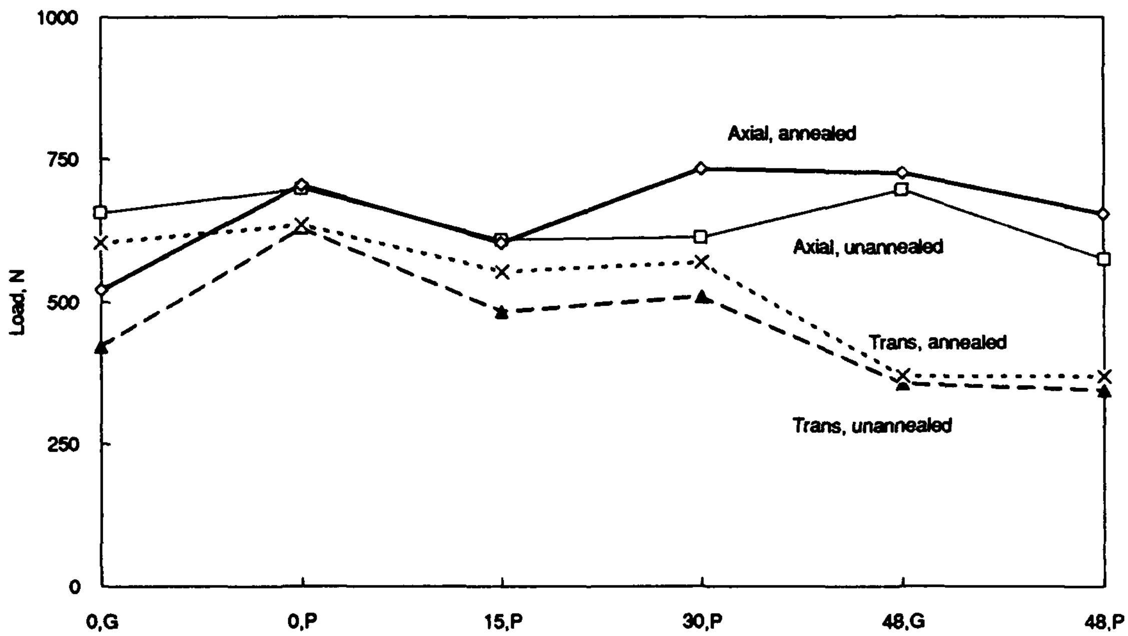


Figure 10: Fracture loads of unnotched propellant bars tested on the drop weight impact tester.

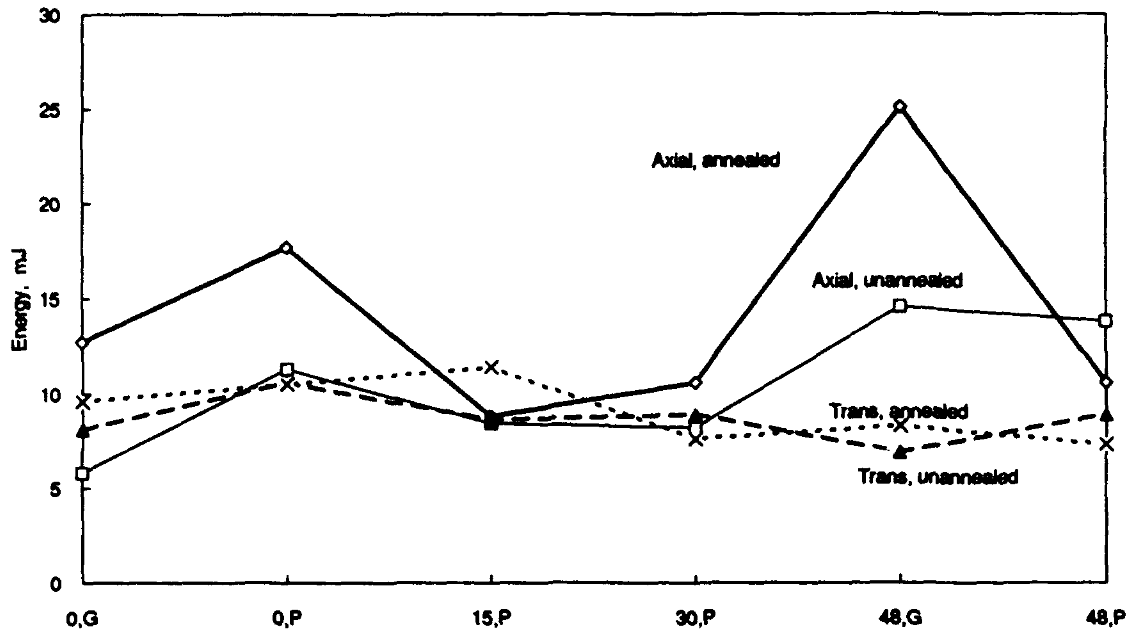


Figure 11: Fracture energies of notched propellant bars tested on the drop weight impact tester.

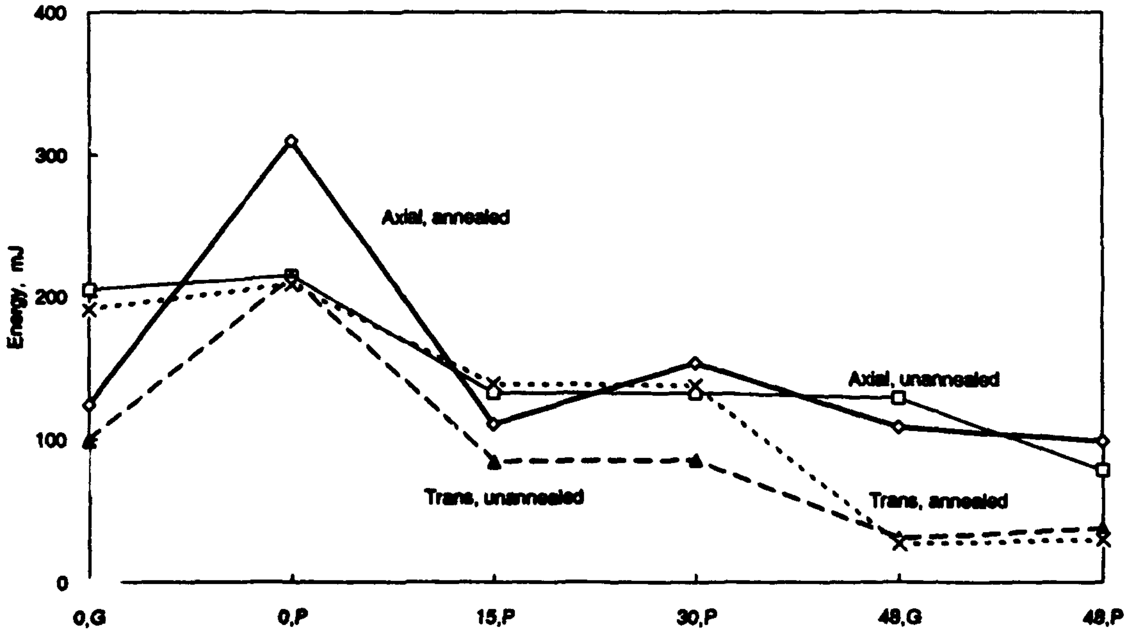


Figure 12: Fracture energies of unnotched propellant bars tested on the drop weight impact tester.

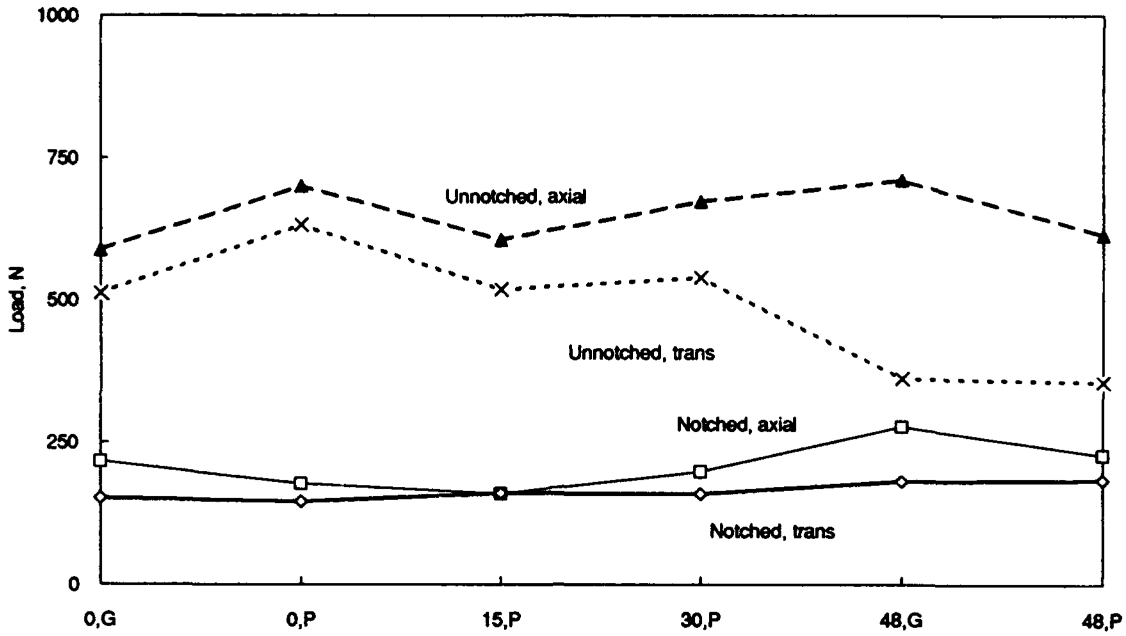


Figure 13: Average of fracture loads of annealed and unannealed propellant bars tested on the drop weight impact tester.

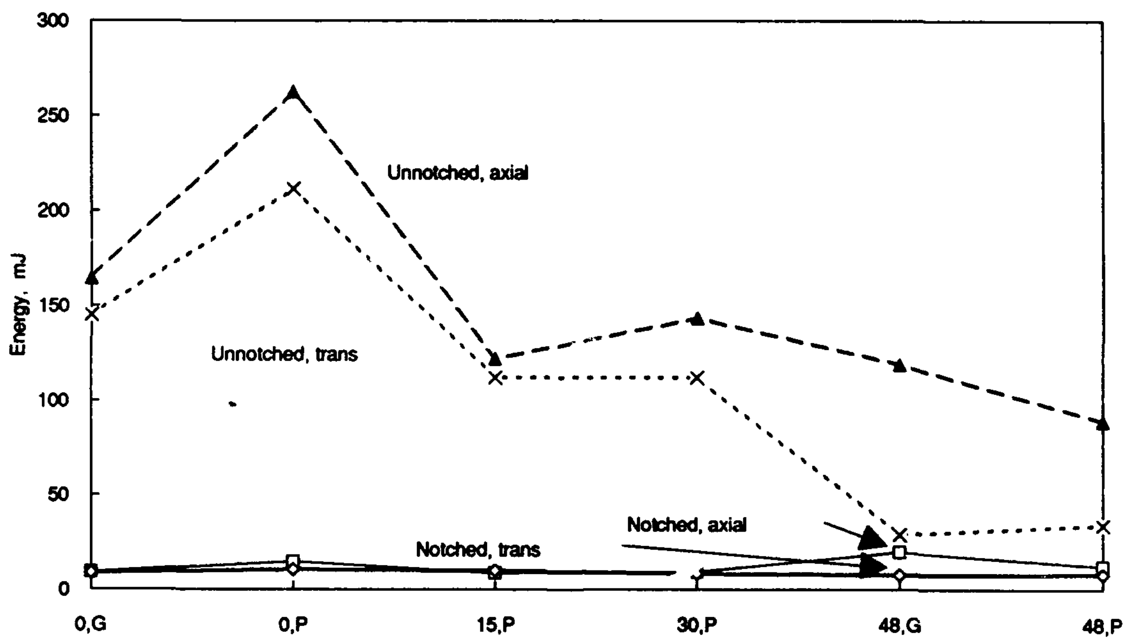


Figure 14: Average of fracture energies of annealed and unannealed propellant bars tested on the drop weight impact tester.

The effect of orientation on the fracture of notched bars was much less pronounced than for the unnotched bars.

5.2.5 *Effect of Notching Bars*

The fracture loads and energies were 2 to 5 times lower for the notched bars than for the unnotched bars, which resulted in a much lower signal to noise ratio in the transducer outputs. In addition the variation of filler content had a smaller effect on the notched bars than the unnotched bars, suggesting that testing notched the bars may not give a good indication of the brittleness of propellants.

6. General Discussion

6.2 General

The response of the propellants to the tests and the effects of the various test parameters are summarised in Table 7, and the overall standard deviations of the results of the tests are given in Table 8. The details and implications of these results will be discussed in the following sections.

***Table 7:** Summary of Effects of Test Parameters on Fracture Behaviour*

	Type of Test				
Parameter	Dynamic Mechanical	Low Rate Grain	High Rate Grain	Notched Bar	Unnotched Bar
Annealing	Very large indicates change of structure	Not conclusive	NA	Not conclusive	Not conclusive
Filler Level	Very large and complex	Significant decrease in toughness at high levels	Increase in fracture load at high levels	Small	Significant decrease in energy with increasing level
Orientation	Large	NA	NA	Small	Large effect in energy, less effect on load
Gelatinisation	Not detectable	Not consistent	NA	Not consistent	Not consistent
Semi-solvent process	NA	More brittle than full solvent, annealing slightly decreases brittleness	NA	NA	NA

NA - indicates not applicable

Table 8: Averaged Percent Standard Deviations of Results

		Load	Energy
	GRAINS		
Single Perforation	Unannealed	8.8	18.2
Single Perforation	Annealed	6.5	15.1
Single Perforation	Unannealed	7.5	15.4
Single Perforation	Annealed	11.4	25.6
Seven Perforation, Drop Bar		8.3	24.9
Overall		8.5	19.8
	NOTCHED BARS		
Axial	Unannealed	8.9	20.2
Axial	Annealed	8.0	18.3
Transaxial	Unannealed	6.9	13.8
Transaxial	Annealed	7.7	15.0
Overall		7.9	16.9
	UNNOTCHED BARS		
Axial	Unannealed	8.1	19.2
Axial	Annealed	5.7	16.8
Transaxial	Unannealed	11.6	33.9
Transaxial	Annealed	5.5	14.1
Overall		7.7	21.0

6.2 *Effect of Annealing*

The surprising result of this work was that annealing produced a large change in dynamic mechanical behaviour(figures 1,2), but it had no clearly discernible effect on the fracture of the grains(figures 5,6) or the notched or unnotched bars(figures 9-12). There is no explanation for this difference in behaviour at present.

6.3 *Effect of Filler Level*

Filler level had a complex series of effects on the results. The greatest effect was on the dynamic mechanical behaviour where modulus increased with increasing filler content and the loss tangent decreased(figures 3,4).

In single perforation grains it was found that the fracture behaviour was essentially constant below a filler level of 30%, but increasing the filler content from 30% to 48 % resulted in a significant loss of toughness(figures 7,8). Seven perforation grains showed the same effect, but to a lesser degree. This result suggests that for situations where propellant grain brittleness is a problem, it may be advisable to use formulations where the filler content is less than about 30%.

Filler level had a very small effect on notched bars and on the fracture load of unnotched bars, but there was a large decrease in fracture energy of the

unnotched bars with increasing filler level(figures 13,14). This observation suggests that testing unnotched bars may give a more sensitive indicator of brittleness than testing notched bars.

6.4 *Effect of Orientation*

The magnitude of the effect of specimen orientation on dynamic mechanical response was large(figures 3,4), but the effect on fracture response of notched bars was found to be quite small(figures 13,14). However, unnotched bars were tougher in the axial direction than in the transaxial direction, and at high filler levels the difference was quite large.

In a grain there would be a high degree of filler and NC molecule alignment in the axial direction, particularly at the surface. Hence a grain would be much weaker when tested in the side on mode where a crack could propagate between the filler particles than in the end-on mode where the filler particles would have maximum reinforcing effect. In the case of ignition of propellant in a gun, propellant grains which happen to be stressed in the side-on orientation would fracture before grains stresses in the end-on orientation. Since the aim is to have no grain fracture, the critical orientation for testing is the side-on, or Trans, mode.

6.5 *Effect of Gelatinisation*

No consistent effect of variation of degree of gelatinisation was found in any of the tests. Since the mixes were "one off" it may be that the processing conditions for the well gelatinised unfilled propellant were not optimised, and it may be possible to produce a tougher well gelatinised propellant. Further work is required to determine the effect of gelatinisation on physical properties.

6.6 *Semi-solvent Process*

The semi-solvent propellant grains were more brittle than their full solvent counterparts(figure 5,6), and this behaviour had been observed previously in tests on bars of MNF2P/S propellants [3]. However, annealing the semi-solvent grains brought their properties closer to the full solvent grains. This behaviour suggests that the NC molecules in the semi-solvent grains were under more internal strain. The effect of annealing would be to partially relieve these stresses and produce an internal structure more like the full solvent propellant. Since it is desirable to use the lowest practicable solvent level to minimise shrinking on drying, further work on the effect of annealing would be justified because it may lead to methods of producing semi-solvent propellants which are as tough as their full solvent counterparts.

6.7 Comparison of Dynamic Mechanical Testing and Fracture Testing

It had been hoped that a correlation could have been found between dynamic mechanical and fracture behaviour, as such a correlation could have been used to devise screening tests to predict fracture behaviour on a routine basis, and this would have reduced the need for full scale fracture testing. However, the results show quite clearly that the dynamic mechanical properties are much more strongly affected by annealing, filler level and orientation than were the fracture properties. It appears that a series of propellants with the same composition could have a range of quite different DMTA traces if they had experienced different thermal histories, and yet all still have similar fracture behaviour.

In these circumstances it is difficult to see how a simple correlation between dynamic mechanical properties and fracture behaviour could be established. This indicates that the relation of molecular behaviour to fracture behaviour is still poorly understood, and the factors which have the most significant effects may still have to be identified.

6.8 Effect of Number of Perforations in the Grains

The fracture of single perforation grains showed a greater sensitivity to the experimental parameters than did the fracture of seven perforation grains(figures 5,6), but there did not appear to be any significant difference in the standard deviations of the loads or energies, see Table 8. Single perforation grains may be useful as a production aid to determine the effect of variations in process parameters, but seven perforation grains are the only type available for testing for propellants in service.

6.9 Drop Bar vs Low Rate Tests

While the fracture loads and energies of the grains tested at low rates on the Instron machine showed a clear drop with increasing filler level, the situation with the high rate drop bar tests was not so clear(figures 7,8). The fracture energy was effectively constant for the triple base propellants and, significantly, the fracture loads for the 48% filled propellants were greater than for all the other propellants. This behaviour requires further investigation, but it indicates that deformation rate is important, and that impact tests may give a better indication of behaviour in the gun than low rate tests.

It is interesting to note that the size of the errors in both tests are comparable (see Table 8) so the variability of the results may not be due to the test, but may be inherent in the propellant.

6.10 Effect of Notching on the Fracture of Bars

The unnotched bars gave larger values of fracture load and energy than the notched bars(figures 13,14). This result is significant because it suggests that the use of unnotched bars would increase the signal to noise ratio of the test, and

hence increase its reproducibility. It is also more relevant to the real system. However, Table 8 shows that the fractional errors of both tests are similar, and this suggests that the variability of the results may be due to real differences in the sample than any deficiency of the test.

The real difference between the notched and unnotched data was in the extra sensitivity of the unnotched fracture energy data to the effect of filler level, orientation, and (possibly) to degree of gelatinisation. The notched bars showed almost no effect of filler or gelatinisation, whereas fracture energy of the unnotched bars showed substantial changes with test parameters.

This result suggests that the most appropriate test for unnotched bars would be one where fracture energy could be measured directly, and not have to be inferred from a load-time trace. These requirements are met by the Charpy pendulum type test.

6.11 Testing of Grains vs Testing of Bars

Notched bars were shown to be much less sensitive to variation in the parameters studied here than were the grains, and so they are likely to be less sensitive to other parameters in general. While the fracture energy of unnotched bars in the Trans direction was moderately sensitive to the variation of parameters, the specimens are difficult and expensive to prepare.

For pilot scale studies where the effect of processing variables on fracture behaviour is to be determined, there is a choice of test specimens between grains and bars. In this case testing propellant grains is to be preferred because it tests the material in the form in which it exists in service. Compressing the grains in the side-on mode across the diameter, as opposed to compressing axially, is to be preferred, because the grains are weakest in this direction, and hence this is likely to be the mode of fracture in the gun. A further advantage is that fracture occurs in a well defined manner. In addition, a minimum of sample preparation is required for grains.

6.12 Magnitude of Errors

The large scatter in the data from all the fracture tests shows the difficulty in obtaining definitive data in this area. Since it appears that the scatter is inherent in the propellant material and not in the test, the best procedure may be to carry out a large number of tests and to quote the results as a mean and standard deviation.

7. Conclusions

Filler level, orientation, and thermal history affected the dynamic mechanical response differently from the fracture behaviour. This observation suggests that the molecular mechanisms involved in the two processes are different, and hence it may not be possible to develop a simple method for prediction of fracture behaviour from dynamic mechanical data.

Filler content had a large effect on the dynamic mechanical properties over the whole range of composition studied. The drop in both modulus and magnitude of the peak in tan δ at temperatures above 50°C decreased significantly in intensity with increasing filler level. However, the effect of filler level on fracture behaviour was much smaller. The fracture loads and energies of grains dropped only slightly as the filler level rose from 0 to 30%, but then dropped significantly when filler level was raised to 48%.

Thermal history had a large effect on the dynamic mechanical response, but no discernible effect on the fracture behaviour of the full solvent processed propellant. However, the annealing of semi-solvent processed propellant increased the fracture loads and energies to values approaching those of full solvent propellants.

The direction of orientation of the specimen relative to the extrusion direction had a large effect on dynamic mechanical response, but a much smaller effect on fracture behaviour.

The semi solvent processed propellant was more brittle that the corresponding full solvent processed propellant, but the difference was decreased by annealing.

The testing of propellant grains is to be preferred to testing machined bars. The form of the propellant in the grains is the same as it is in the gun, and so the results of grain testing can be more closely related to performance in the gun. A further advantage is that a minimum of sample preparation is required. The side on mode, rather than the end on mode, should be used because it gives a well defined fracture event, and fracture in this mode is the most likely to occur in the gun.

If impact testing of bars is required, then testing unnotched bars is to be preferred. The fracture loads and energies of the unnotched bars were considerably greater than the values for notched bars, and this increased the accuracy of the test results. The fracture energy was relatively sensitive to changes in processing parameters.

8. Acknowledgements

The author would like to acknowledge Mr. S. Odgers for the manufacture of the propellants, Mr W. Stevens for much of the testing, and Mr D. Kirk for software development.

9. References

1. Fong, C.F. and Warren, R.C. (1985). The Effect of Filler Particle size and Orientation on the Impact Fracture Toughness of a Highly Filled Plasticised Polymeric Material. *J.Mat.Sci.*, 20, 3101

2. Warren, R.C. (1985). Impact Fracture Behaviour of Double Base Gun Propellants. *J. Mat.Sci.*, 20, 3131

3. Warren, R.C., Odgers, S.O. and Fong, C.W. (1987). The Deleterious Effect of Roll Milling on the Mechanical Properties of a Triple Base Gun Propellant. Proceedings of 1987 ICT Conference, Karlsruhe, FRG.

4. Kinloch, A.J. and Gledhill, R.A. (May 1980). Mechanics of Crack Growth in Double Base Propellants. International Conference on Nitrocellulose Characterisation, Propellants, Explosives and Rocket Motor Establishment, Waltham Abbey, UK, .

5. Baker, F.S. and Privett G.J. (1987). Dynamic Mechanical Studies of Nitrocellulose/Nitroglycerine Mixtures", *Polymer*, 28, 1121

6. Warren, R.C. (1990). The Effect of Ageing and Annealing on the Physical Properties of Nitrocellulose Plasticised with Nitroglycerine. *Polymer*, 31, 861

7. Warren, R.C. and Starks, A.T. (1988). *Multiple Flow Regimes in the Extrusion of Nitrocellulose Based Propellant Doughs*. WSRL Technical Report TR-43/88.

8. Townend, D.J. and Warren, R.C. (1985). Relaxations in Double Base Propellants. *Polymer*, 26, 79

9. Fong, C.W. and Warren, R.C. (1985). An Interphasic Region between Nitrocellulose and Nitroglycerine in a Triple Base Propellant. *Propellant, Explosives and Pyrotechnics*, 10, 69

REPORT NO.	AR NO.	REPORT SECURITY CLASSIFICATION
MRL-TR-93-40	AR-008-570	Unclassified

TITLE

Dynamic mechanical and fracture properties of some double and triple base gun propellants

AUTHOR(S)
R.C. Warren

CORPORATE AUTHOR
DSTO Materials Research Laboratory
PO Box 50
Ascot Vale Victoria 3032

REPORT DATE	TASK NO.	SPONSOR
March, 1994	NAV 91/375	RAN

FILE NO.	REFERENCES	PAGES
G6/4/8-4325	9	35

CLASSIFICATION/LIMITATION REVIEW DATE

CLASSIFICATION/RELEASE AUTHORITY
Chief, Explosives Ordnance Division

SECONDARY DISTRIBUTION

Approved for public release

ANNOUNCEMENT

Announcement of this report is unlimited

KEYWORDS

Gun propellants
Grain compression
Propellant grains
Perforated propellant grains

ABSTRACT

Dynamic mechanical tests and two types of fracture test were carried out on gun propellants of a range of compositions and made by different processes. Double base propellants, and triple base propellants containing 15%, 30% and 48% picrite, were made by the full solvent process, and one triple base propellant containing 48% picrite was made by the semi-solvent process. Dynamic mechanical and impact fracture tests were carried out on machined bars and low rate compression tests were also carried out on grains. The propellants were tested in both the as-received state and also after annealing and ageing. Filler content and annealing were found to have a large effect on the dynamic mechanical properties but these factors had a much smaller effect on fracture behaviour. No correlation between the results of dynamic mechanical measurements and fracture tests could be found. Propellant grain testing appeared to give more reliable fracture data than the impact testing of bars.

Dynamic Mechanical and Fracture Properties of Some Double and Triple Base Gun Propellants

R.C. Warren

(MRL-TR-93-40)

DISTRIBUTION LIST

Director, MRL - title page only
Chief, Explosives Ordnance Division
Dr R.J. Spear
Mr R.C. Warren
MRL Information Services

Chief Defence Scientist (for CDS, FASSP, ASSCM)	1 copy only
Director (for Library), Aeronautical Research Laboratory	
Head, Information Centre, Defence Intelligence Organisation	
OIC Technical Reports Centre, Defence Central Library	
Officer in Charge, Document Exchange Centre	8 copies
Air Force Scientific Adviser, Russell Offices	
Navy Scientific Adviser	
Scientific Adviser - Policy and Command	
Senior Librarian, Main Library DSTOS	
Librarian, H Block	
Serials Section (M List), Deakin University Library, Deakin University, Geelong 3217	
NAPOC QWG Engineer NBCD c/- DENGRS-A, HQ Engineer Centre, Liverpool Military Area, NSW 2174	
ABCA, Russell Offices, Canberra ACT 2600	4 copies
Librarian, Australian Defence Force Academy	
Head of Staff, British Defence Research and Supply Staff (Australia)	
NASA Senior Scientific Representative in Australia	
INSPEC: Acquisitions Section Institution of Electrical Engineers	
Head Librarian, Australian Nuclear Science and Technology Organisation	
Senior Librarian, Hargrave Library, Monash University	
Library - Exchange Desk, National Institute of Standards and Technology, US	
Exchange Section, British Library Document Supply Centre	
Periodicals Recording Section, Science Reference and Information Service, UK	
Library, Chemical Abstracts Reference Service	
Engineering Societies Library, US	
Documents Librarian, The Center for Research Libraries, US	
Army Scientific Adviser, Russell Offices	
Director General Force Development (Land)	
DASD, APW2-1-OA2, Anzac Park West, Canberra ACT - data sheet only	
SO (Science), HQ 1 Division, Milpo, Enoggera, Qld 4057	
Librarian - MRL Sydney - data sheet only	
Counsellor, Defence Science, Embassy of Australia - data sheet only	
Counsellor, Defence Science, Australian High Commission - data sheet only	
Scientific Adviser to DSTC Malaysia, c/- Defence Adviser - data sheet only	
Scientific Adviser to MRDC Thailand, c/- Defence Attache - data sheet only	

DARMENG-N
RAN Gun Propellant Management Authority (RSNES-M)
Mr J.F. Hooper, EOD-S
Mr N.V. Ayres, EOD-S
Mr S.G. Odgers, EOD-S
Mr S.P. Cashion, EOD-S
Dr S.Y. Ho, EOD-S